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Selective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde over nickel-carbon composite catalyst

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Methane is decomposed to carbon and hydrogen over Raney nickel catalyst in controlled manner in order to deposit carbon; and thereby NiC composite catalysts have been prepared. The catalysts have been analyzed by atomic emission spectroscopy, X-ray photoelectron spectroscopy and X-ray diffraction. The NiC catalysts are comprised of metallic nickel with superficial oxide and carbon. Electron density of Ni in the NiC catalysts is observed to be higher than that in the parent Raney nickel; this indicate partial charge transfer from carbon to nickel in the NiC catalysts. The NiC catalysts exhibite much better performance than the original Raney nickel catalyst in the selective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde. They also exhibite stable performance in multiple reaction runs.

Keywords: Charge transfer, Cinnamaldehyde, Hydrogenation, Hydrocinnamaldehyde, NiC catalyst

Selective hydrogenation of a particular functional group that is present in a molecule containing multiple reducible groups is of great interest from academic as well as applied point of view[1-13]. α, β-Unsaturated aldehydes are such type of molecule, containing two reducible groups that can be hydrogenated – an olefinic function and an aldehyde group. Hydrogenation at olefinic function results in saturated aldehyde, whereas that at aldehyde group leads to unsaturated alcohol. On the other hand, complete hydrogenation i.e., hydrogenation of both the functions results in saturated alcohol. The selectivity of products depends on reaction conditions as well as on the properties of the catalyst that is used. In the hydrogenation of an unsaturated aldehyde, thermodynamics favours hydrogenation of the $C = C$ double bond over that of the aldehyde group[3]. Inspite of that, there is always some probability of the reduction of the aldehyde group. Hence, selective hydrogenation of the C=C function in an unsaturated aldehyde to obtain high yield of saturated aldehyde is certainly of great interest. Catalytic hydrogenations are better choice over the non-catalytic ones because of environmental restrictions. Large amount of waste is produced in non-catalytic process, whereas catalytic process produces minimal amount. As a result, catalytic processes are replacing non-catalytic ones to cope in the environmental regulations.

Supported noble metals and nickel, particularly Raney nickel, catalysts are widely used in hydrogenation of carbon – carbon multiple bonds. However, noble metals are scanty and precious. Therefore, considering the cost and availability, cheap and abundant metals like nickel can be a good option[7,8,14]. Nickel, particularly Raney nickel catalysts are used both in the laboratory and in industry; low cost and acceptable performance make them attractive. However, Raney nickel catalyst has serious drawbacks. They are potentially pyrophoric; hence, need extra care for handling, storage and transportation. Also, they readily deactivate when exposed to air. Mahata and co-workers have developed a methodology to stabilize Raney nickel by controlled carbon deposition; and thereby to synthesize NiC composite material[7,8]. The methodology involves decomposition of methane, to carbon and hydrogen, in controlled manner over Raney nickel. The deposited carbon strongly interacts with nickel; a part diffuses through the metal. The NiC composite materials have been found to be excellent catalyst for hydrogenation of reducible functions like $C = C$ double bond, NO_2 group, etc[7,8]. They are stable; can be stored under air for prolonged times without losing activity. NiC composite material seems to be very interesting system; further studies are required on this system.

Products of cinnamaldehyde hydrogenation, hydrocinnamaldehyde and cinnamyl alcohol, are very important and useful. They find wide applications in pharmaceutical, perfume and fine chemical industries[1-6,9-12]. Hydrocinnamaldehyde is an important compound used in synthesizing a HIV drug[1,10,15,16]. Reports on hydrogenation of cinnamaldehyde to hydrocinnamaldehyde with acceptable selectivity are scanty[4-6,14]. NiC catalysts are prepared from Raney nickel and their catalytic performance in the selective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde is explored in the present study.

Experimental Section

Catalysts preparation

Raney nickel (RNi) catalysts were synthesised from a Ni-Al commercial alloy (Ni/Al = 50/50 w/w). Methane was decomposed in controlled manner over the RNi catalysts to deposit carbon; and thereby NiC composite materials were obtained[7,8].

In a typical synthesis, Al was leached out from Ni-Al alloy reacting with concentrated NaOH solution at ambient temperature for 4 h. Subsequently, the RNi catalyst was washed several times sequentially with distilled water and ethanol. The RNi was then taken carefully into a tubular reactor avoiding exposure to air and dried at 353 K in nitrogen flow (50 cm^3 min^{-1}) for 3 h. Methane was decomposed over the RNi catalyst in controlled manner at 665 K (space velocity of methane: 12 cm^3 min^{-1} g^{-1} Ni) for a particular period of time; carbon was deposited avoiding severe rupture of the skeletal structure of Ni. Nickel-carbon composite catalyst (NiC catalyst) was thus synthesized. Finally, the reactor was cooled to ambient temperature under nitrogen flow and the catalyst was collected. Four NiC catalysts- NiC-4, NiC-8, NiC-10 and NiC-15, were synthesized by varying the period of time of methane decomposition reaction. The numerals (4, 8, 10, and 15) in designating the catalysts indicate the duration of methane decomposition in hours.

Catalysts characterization

The catalysts were characterised applying several physico-chemical techniques. Nickel content was determined by atomic emission spectroscopy. Deposited carbon in the NiC catalysts was determined gravimetrically as follows. NiC material was subjected to prolonged treatment with hot concentrated NaOH solution to dissolve residual aluminium metal/hydroxide/oxide, then filtered and washed with distilled water. The residue was subsequently treated with dilute nitric acid to dissolve nickel metal/hydroxide/oxide. The final residue (carbon) was filtered, washed thoroughly with distilled water, dried well and weighed. X-ray photoelectron spectroscopy (XPS) analyses were carried out applying Mg K_α radiation (1253.6 eV) to examine the chemical state of surface Ni in the catalysts. X-ray diffraction (XRD) measurements were conducted applying Cu K_α radiation (0.154 nm). N_2 adsorption isotherms over the catalysts were measured at 77 K to determine the surface area by BET method.

Hydrogenation of cinnamaldehyde

Hydrogenation of cinnamaldehyde (CMD) was carried out in a custom made stainless steel reactor at 393 K under 1.5 MPa of H_2, using ethyl acetate as solvent. In a typical experiment, calculated amounts of CMD, catalyst, and solvent were put into the reactor and purged 5 times with H_2 at a pressure of 0.5 MPa. Then the reactor was heated to reaction temperature, 393 K, at a heating rate of 20 K min^{-1} under 0.1 MPa H_2. Finally, the pressure of H_2 was adjusted to reaction pressure (1.5 MPa) and stirring of reaction mixture was started to initiate the reaction.

Periodically, aliquots of liquid samples were collected and analysed chromatographically to determine CMD conversion and product selectivities. Conversion of CMD and selectivity of products were calculated as follows:

Conversion of CMD (%) = [1 − {concentration of CMD / (concentration of all products + concentration of CMD)}] × 100%.

Selectivity of product, **P** (%) = (concentration of **P** / concentration of all products) × 100%.

Results and Discussion

Characterisation of catalysts

The amount of nickel in the catalysts were determined by atomic emmision spectroscopy. The Ni amounts (wt%) were found as:- RNi: 88.7; NiC-4: 84.9; NiC-8: 80.6; NiC-10: 78.8; NiC-15: 76.8. The amount of deposited carbon in the NiC catalysts was assessed gravimetrically. Wt% of carbon in the NiC catalysts was found to be as follows:- NiC-4: 3.7; NiC-8: 7.8; NiC-10: 9.5 and NiC-15: 11.8. As expected, the amount of deposited carbon increases with increase in duration of methane decomposition reaction.

The catalysts were examined by XPS analysis to assess the chemical state of surface Ni. Fig. 1 shows the Ni $2p_{3/2}$ photoelectron spectra exhibited by the catalysts. It is clearly evident from the spectra that surface Ni is existed in metallic (Ni^0) and oxidised (Ni^{+2}) forms in all the catalysts. Photoelectron peaks at binding energy (BE) values of 852.99 ± 0.09 eV correspond to Ni^0 and peaks at 856.62 ± 0.14 eV correspond to Ni^{+2} in the NiC catalysts[7,8,14]. Likewise, peak at 853.42 eV corresponds to Ni^0 and a weak hump at 856.78 eV corresponds to Ni^{+2} in the original RNi catalyst.

It is interesting to observe that binding energy (BE) of Ni^0 in the NiC catalysts shifted to lower values (852.90 – 853.08) compared to that in the RNi (853.42 eV)[7,8]. Ni^0 binding energy values are listed in Table 1. Shifting of BE of Ni^0 in the NiC catalysts to lower values compared to the parent RNi clearly indicates partial electron transfer from carbon to nickel[7,8,17,18]. In other words, electron density of Ni in NiC is higher than that in RNi. XRD analysis (shown below) confirmed the presence of carbon in the NiC catalysts.

The catalysts were also examined by XRD. Difraction patterns are shown in Fig. 2. It is evident from the spectra that nickel is existed in crystalline metallic form in all the catalysts. XRD peaks at 2θ value of 44.52° correspond to Ni(111), peaks at 51.74° correspond to Ni(200), and peaks at 76.54° correspond to Ni(220)(Refs 7,8,17-20). Diffraction peak at 2θ value of 26.24° confirms the presence of graphitic carbon, C (002), in the composite catalysts[7,8,14,20-22]. The peak is clearly visible in the diffractograms of all the NiC catalysts except that of NiC-4. However, presence of some amorphous carbon cannot be ruled out as the methane was cracked at relatively lower temperature[7]. Nonappearance of distinct C(002) peak in case of NiC-4 may be due to lower extent and/or amorphous nature of the deposited carbon. Nickel is stabilised, in metallic form, by carbon in the NiC catalysts. No peak corresponding to oxidised nickel (oxide / hydroxide) was detected. This observation apparently appears to be contradictory to the XPS results. However, in reality it is not. A very small amount of superficial nickel oxide / hydroxide exists on the surface (evidenced by XPS), which is below the detection range of XRD[7,8].

Surface areas of the catalysts were determined by applying BET method on N_2 adsorption isotherms measured at 77 K. The BET surface area ($m^2\ g^{-1}$) of the catalysts was found to be as:- RNi: 82; NiC-4: 92; NiC-8: 97; NiC-10: 99; NiC-15: 103.

Table 1 — Analysis of Ni $2p_{3/2}$ XPS spectra

Catalyst sample	Ni^0 Binding energy (BE) (eV)
RNi	853.42
NiC-4	853.02
NiC-8	852.96
NiC-10	852.90
NiC-15	853.08

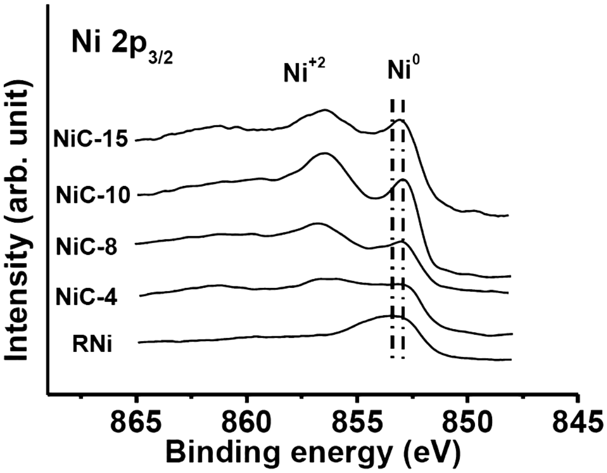


Fig. 1 — Ni $2p_{3/2}$ XPS spectra of NiC and parent RNi catalysts.

Hydrogenation of cinnamaldehyde

The hydrogenation of cinnamaldehyde (CMD) mainly results in hydrocinnamaldehyde (HCMD), cinnamyl alcohol (CML) and 3-phenyl propanol (PPL). Plausible reaction pathways are shown in Scheme 1[2,9,10]. Addition of hydrogen selectively to C = C function results in HCMD, that to >C = O group results in CML, while PPL is formed as a result of

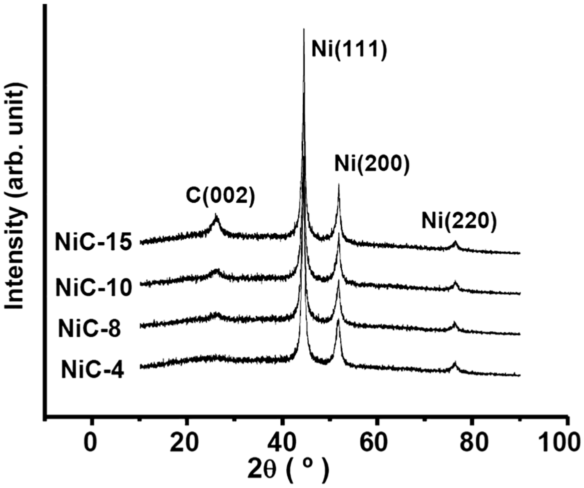
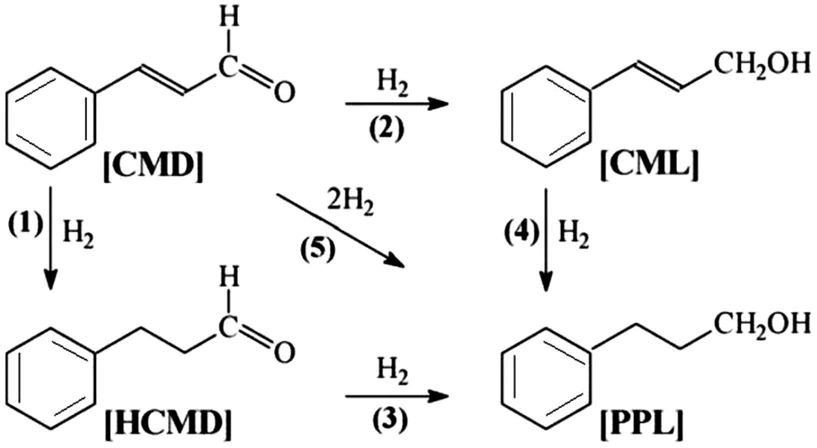


Fig. 2 — XRD spectra of the NiC catalysts.



Scheme 1 — Reaction pathways in CMD hydrogenation.

hydrogenation of both the reducible functions.

Blank reaction (solvent + CMD + 1.5 MPa H_2) run, in absence of catalyst, was carried out at 393 K (reaction temperature) for over 8 h; no CMD conversion was detected. Hence, contribution of non-catalytic path can be ruled out in the present study.

The reaction time versus CMD conversion profiles over the catalysts are shown in Fig. 3 to focus on their activity. Performances of the NiC catalysts are much better than that of the original RNi. Complete conversion of CMD over the RNi catalyst is achieved in 800 min. Whereas, the corresponding times over the NiC catalysts are: NiC-4 – 400 min, NiC-8 – 250 min, NiC-10 – 260 min, NiC-15 – 315 min. Selectivity of HCMD at complete conversion of CMD was found to be as: RNi – 83%, NiC-4 – 86%, NiC-8 – 87%, NiC-10 – 87%, NiC-15 – 87%. Needless to mention that HCMD selectivity was higher than these values at lower CMD conversion. Selectivity of HCMD over RNi remains almost constant (at 93 – 94%) up to ~ 75% CMD conversion and then drops rapidly (to 83% at 100% CMD conversion). On the other hand, HCMD selectivity over the NiC catalysts drops gradually (from 97 – 98% to 86 – 87%) with increase in CMD conversion. In concise, the NiC catalysts exhibited excellent HCMD selectivity, better than the RNi throughout the full domain of conversion (1 – 100%).

Liu *et al.* reported 88% HCMD selectivity at 100% CMD conversion over multi-walled carbon nano tube supported Pt catalyst4, while Li *et al.* have reported 88% HCMD selectivity at 99% CMD conversion over carbon nano tube supported bimetallic Pt-Ni catalyst[5]. On the other hand Xie *et al.* have reported 94.8% HCMD selectivity at 100% CMD conversion over grapheme supported nano Ni catalyst prepared involving Ni-Al layered double hydroxide precursor[14]. HCMD selectivity in the present study is comparable to these studies. However, considering the easiness of catalyst synthesis at the same time involving cheap metal (Ni), the present study is expected to attract attention of researchers from academic as well as industrial sector. Along with HCMD, the only other product was PPL in the present study; no CML was detected at any level of conversion. Similar results have been observed by Gryglewicz *et al.* over Ni catalyst supported on carbon nano fibre and activated carbon[23]. Tessonnier *et al.* also have reported similar observation over carbon nano tube supported Pd catalyst[24].

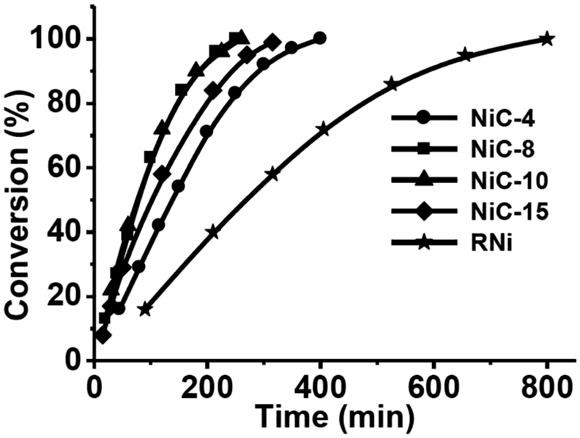


Fig. 3 — CMD conversion profiles with reaction time exhibited by the NiC and original RNi catalysts. Reaction conditions: catalyst containing 1 mmol Ni, 6.3 mL (50 mmol) CMD, 94 mL ethyl acetate (solvent), 1.5 MPa H_2, 393 K, 1100 rpm.

Product selectivity and yield were plotted against CMD conversion to assess how they behave with change in CMD conversion. Representative profiles exhibited by NiC-8 and RNi are shown in Fig. 4. Important information can be extracted from Fig. 4. Variation of respective product selectivities with CMD conversion over NiC-8 and RNi follows different paths; data points produced by NiC-8 and RNi fall on distinctively different smooth curves. This clearly indicates that the nature of active site on NiC-8 is different than that on RNi. This is in accordance to XPS results. It is evident from XPS results that electron density of Ni in NiC is significantly different than that in RNi. Thus, it can be inferred that electron density over Ni has significant influence on product selectivity.

Catalyst stability in multiple successive runs in liquid phase reactions is an important issue. A viable catalyst performs with good stability in activity in successive runs. All the NiC catalysts were subjected to multiple successive reaction runs; fairly stable activity was exhibited by all of them. Successive multiple reaction runs over NiC-8 are shown in Fig. 5 as representative. It can be seen that the successive reaction profiles are almost super imposable; no significant loss in activity was observed. Hence, the NiC composite catalysts can be applied successfully in multiple runs.

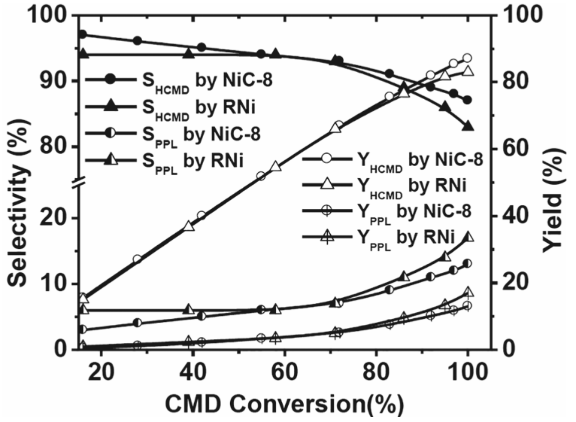


Fig. 4 — Variation of product selectivities (S...) and yields (Y...) with CMD conversion over NiC-8 and original RNi catalysts. Reaction conditions: same as given in Fig. 3.

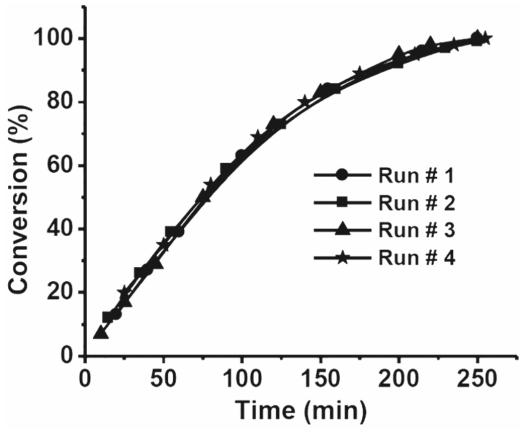


Fig. 5 — CMD conversion profile with reaction time in successive multiple runs exhibited by NiC-8. Reaction conditions: same as given in Fig. 3.

Catalytic activity was tried to correlate to BET surface area of the catalysts. However, no smooth/meaningful correlation was found. Probably, available Ni sites and charge density on Ni are dominating factors.

Following reasoning may be invoked to explain the better activity of the NiC catalysts compared to the parent RNi. Carbon has been deposited on RNi by means of controlled methane decomposition; thereby NiC catalyst has been synthesized. The carbon diffuses through Ni and inevitably develops cracks in the skeletal structure[7,8,25]. The cracks generate new catalytic site. The number of additional sites likely surpasses the number of sites blocked by the deposited carbon. The net gain in catalytic sites may be accounted for the enhanced activity of the NiC catalysts[7,8]. The activity of the NiC catalysts varies in the order: NiC-4 < NiC-8 ≈ NiC-10 > NiC-15. It is clear that optimum amount of carbon deposition leads to the most active catalyst. Excess carbon deposition during catalyst synthesis by means of methane decomposition for prolonged period of time is proved to be detrimenta[l8]. The higher HCMD selectivity over the NiC catalysts may be attributed to the higher electron density of the Ni sites. XPS analysis (Fig. 1 and Table 1) shows decrease in BE of Ni^0 in the NiC catalysts compared to the RNi. This clearly indicates partial electron transfer from deposited carbon to nickel resulting in higher electron density over Ni in NiC compared to that in RNi. Consequently, Ni with higher electron density repulses the negative part i.e., the –CHO group of CMD; thereby restricting adsorption through –CHO and facilitating adsorption through the C = C function. Thus, subsequent hydrogenation results in higher selectivity of HCMD[18,26].

Conclusion

NiC composite catalysts were synthesised by means of decomposing methane to carbon and hydrogen in controlled manner over skeletal Raney nickel.

The NiC composites were found to be excellent catalyst, superior to the original Raney nickel, for the selective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde.

Additional catalytic sites at the cracks, developed in the skeletal structure of Ni by the diffused carbon, are accounted for the superior activity of the NiC catalysts. Product distribution was significantly influenced by electron density of Ni. Higher HCMD selectivity over the NiC catalysts is attributed to higher electron density over Ni.

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